

## Method Development for the Simultaneous Quantification of Mercury and Tin Species in Sediment and Tissue SRMs

*Methods applicable to speciation of mercury and organotin in biological reference materials using speciated isotope dilution-gas chromatography-inductively coupled plasma-mass spectrometry (SID-GC/ICP-MS) have been developed and optimized. These methods were applied to measurement of methylmercury, inorganic mercury, and mono-, di-, and tributyltin species in sediment and tissue Standard Reference Materials (SRMs).*

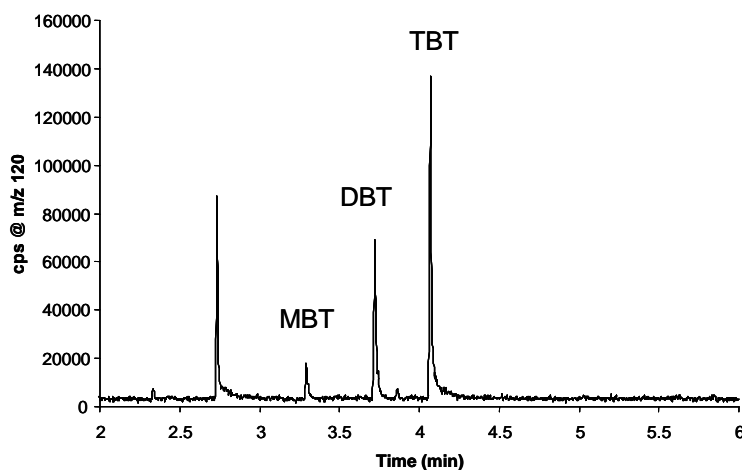
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**T**ributyltin (TBT) and its degradation products, dibutyltin (DBT) and monodibutyltin (MBT), are toxic compounds widely dispersed in the environment. TBT has been used as a biocide in marine antifouling paints since the 1970s. Its release into the marine environment has resulted in extensive damage to organisms such as oysters and mussels. In the case of mercury, the environmental and human health effects are generally related to the environmental transformation of inorganic mercury to toxic methylmercury, and subsequent bioaccumulation of methylmercury in wildlife and humans. In some cases, more than 90% of the total mercury found in edible fish tissue is in the form of methylmercury. The potential for human and environmental impacts calls for improvements in current analytical methods to obtain accurate measurements for specific organometallic species.

Most methods for the analysis of organometallic species are based on hyphenated instrumental techniques in which the species are first separated by gas or liquid chromatography and then detected by ICP-MS. Our recent research has centered on the implementation of advanced calibration procedures that yield accurate results suitable for the certification of SRMs. Despite significant improvements in methods and instrumentation, transformation of mercury species during sample preparation may occur. The transformations can result in significant bias in the measurement of mercury species. For this reason, a double-spike speciated isotope dilution (DS-SID) method has been implemented using a methylmercury ( $\text{CH}_3^{202}\text{Hg}$ ) spike (CRM AE670, Institute of Reference Materials and Measurements) in concert with inorganic mercury ( $^{201}\text{Hg}^{+2}$  spike, Oak Ridge National Laboratory) for the simultaneous determination of both species. A reaction model has also been developed to correct for the possible transformations affecting methylmercury and inorganic mercury measurements in biological tissues. This method is now

being used to measure mercury species in both marine biota and sediment SRMs.

In addition, a SID method was developed for the quantitation of MBT, DBT, and TBT in SRM 1974b Organics in Mussel Tissue (*Mytilus edulis*). These are the first values assigned for organotins in a cryogenic fresh-frozen SRM at low concentrations. Multiple methods were compared using varying extraction conditions to check for potential butyltin species degradation. No statistically significant differences were observed between the extraction methods for the individual organotin species.



*GC/ICP-MS determination of mono-, di-, and tributyltin in SRM 1974b Organics in Mussel Tissue (*Mytilus edulis*).*

### **Future Plans:**

Measurements of mercury and butyltin species in SRM 1974b will continue to assess the stability of these analytes at storage temperatures of  $-80^{\circ}\text{C}$ .